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(54) Title of the Invention:

AQUEOUS POLYURETHANE EMULSIONS AND A METHOD FOR THEIR PRODUCTION

(21) Application No.: 55[1980]-61,717

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## S P E C I F I C A T I O N

### 1. Title of the Invention

### AQUEOUS POLYURETHANE EMULSIONS AND A METHOD FOR THEIR PRODUCTION

### 2. Scope of the Patent Claim(s)

(1) Aqueous polyurethane emulsions, characterized in that they are composed of water and a polyurethane which is a reaction product of

- (a) a polyhydroxy compound that contains at least 3 functional groups;
- (b) a monohydroxy polyalkylene oxide with a molecular weight of 400-8,000 in which 50-100% by weight of the polyoxyalkylene chain is an oxyethylene chain;
- (c) a polyisocyanate; and
- (d) a chain extender.

(2) Method for the production of aqueous polyurethane emulsions, characterized in that (a) a polyhydroxy compound that contains at least 3 functional groups and (b) a monohydroxy polyalkylene oxide with a molecular weight of 400-8,000 in which 50-100% by weight of the polyoxyalkylene chain is an oxyethylene chain are reacted with an excess of (c) a polyisocyanate to form substantially an isocyanate-terminated prepolymer, followed by either dispersing in water with subsequent reaction with (d) a chain extender, or partially extending the chain of the prepolymer with a chain extender, followed by dispersing in water and then reaction with (d) a chain extender.

### 3. Detailed Description of the Invention

The present invention pertains to solvent-free aqueous polyurethane emulsions and a method for their production. Generally speaking, polyurethanes have excellent elasticity, weatherability, water resistance, chemical resistance, etc., therefore they have been used as coating materials for paper and cloth, paints, the coating of metals, synthetic leathers, adhesives, etc. So far, mainly solution-type polyurethanes have been used. However, because their odor, toxicity, inflammability, etc., tend to negatively affect the workplace environment and/or from the standpoint of workability, there is a strong demand for the use of aqueous polyurethanes.

So far, various investigations of aqueous emulsions of polyurethane (or polyurethane polyurea) have been carried out. For example, (A) those obtained using an emulsifier and (B) those obtained by introducing quaternary ammonium salts, carboxyl groups, sulfonic acid groups, and their salts, which are ionic groups that are soluble in water, are known. However, for those obtained in general using emulsifiers in accordance with method (A), it is difficult to obtain emulsions with sufficient stability. And in order to obtain a sufficiently stable emulsion, it is necessary to use a large amount of emulsifier, which may lead to a reduction in the quality of the polyurethane. And when polyurethane is used in the production of artificial leather, a dyeing process must be employed. However, when an aqueous polyurethane emulsion prepared by using a large amount of emulsion is used, sometimes the emulsifier appears in the dyeing solutions in the dyeing process so that foaming becomes vigorous, the texture "floats", thus the workability becomes poor. Next, in the method (B) in which ionic groups are introduced into the polyurethane, the reaction is complicated, and at the time of synthesizing the prepolymers, sometimes the use of a solvent is necessary to help in the dissolution of the ionic groups. However, in this case a process is needed to remove the solvent. When an aqueous polyurethane emulsion that contains a solvent is used to produce artificial leather from multi-component composite fibers made of poly(ethylene terephthalate) as a "multiple island" constituent and polystyrene as a "sea" constituent, the polystyrene is invaded by the solvent so that the nonwoven fabrics, woven fabrics, knitted goods, etc., are degraded, therefore a bulky artificial leather cannot be obtained. In addition to (A) and (B), composition (C) is also known and is produced by introducing hydrophilic polyalkylene oxide polyether chains and ionic groups into polyurethane to give an electrolyte-containing polyurethane. In this case, it has the same drawbacks as (B) mentioned above and there is a handling problem due to its sensitivity to heat. What is more, because it contains electrolytes, containers made of iron can be corroded.

The present inventors carried out an extensive study on high-quality aqueous polyurethane emulsions for use in artificial leather, etc., and as a result it was found that an emulsifier could be omitted, and when an emulsifier was used, only a very small amount was necessary. The present invention, which provides aqueous polyurethane emulsions and a method for their production, was developed on the basis of this discovery.

Namely the present invention pertains to

(1) aqueous polyurethane emulsions, characterized in that they are composed of water and a polyurethane which is a reaction product of

- (a) a polyhydroxy compound that contains at least 3 functional groups;
- (b) a monohydroxy polyalkylene oxide with a molecular weight of 400-8,000 in which 50-100% by weight of the polyoxyalkylene chain is an oxyethylene chain;
- (c) a polyisocyanate; and
- (d) a chain extender.

Furthermore, the present invention pertains to

(2) A method for the production of aqueous polyurethane emulsions, characterized in that (a) a polyhydroxy compound that contains at least 3 functional groups and (b) a monohydroxy polyalkylene oxide with a molecular weight of 400-8,000 in which 50-100% by weight of the polyoxyalkylene chain is an oxyethylene chain are reacted with an excess of (c) a polyisocyanate to form substantially an isocyanate-terminated prepolymer, followed by either dispersing in water (with a small amount of an emulsifier if necessary) and either subsequent reaction with (d) a chain extender or partially extending the chain of the prepolymer with a chain extender, followed

by dispersing in water (with a small amount of an emulsifier if necessary) and then reaction with (d) a chain extender.

The "number of functional groups" means "the number of hydroxy groups per molecule". For a mixture, it is the value obtained by dividing the total number of hydroxy groups by the total number of molecules.

The polyhydroxy compound with at least 3 functional groups used in the aqueous polyurethane emulsion of the present invention has a molecular weight of at least 92, and preferably from 92 to about 8,000, and those which are typically used in the production of polyurethane can be used. Representative examples include polyethers produced by the addition polymerization of at least one compound selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, and cyclohexylene oxide in the presence of at least one compound with at least 3 active hydrogen atoms, such as glycerol, trimethylolpropane, sucrose, sorbitol, etc., as an initiator and a common method [see **Revision 1**]; polyesters prepared by ring-opening polymerization of at least one cyclic ester, such as d-valerolactone, e-caprolactone, etc., in the presence of an initiator with at least 3 hydroxy groups; low-molecular-weight compounds, such as glycerol, trimethylolpropane, etc.; however, the present invention is not limited to these compounds.

In addition to (a) a polyhydroxy compound with at least 3 functional groups, known polyhydroxy compounds which are typically used in the production of polyurethane and have 2 or more but less than 3 functional groups and a molecular weight of 62 or greater, and preferably at least 62 up to about 8,000 or less can be used. Representative examples include polyethers which can be produced by addition polymerization of at least one compound selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, cyclohexylene oxide, etc., using a common method in the presence of at least one compound that has two active hydrogen atoms, such as ethylene glycerol, diethylene glycol, tetramethylene glycol, hexamethylene glycol, neopentyl glycol, etc., as an initiator, and in addition, those obtained by the dehydration condensation of at least one compound that contains at least 2 hydroxy groups selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, butanediol, neopentyl glycol, hexanediol, glycerol, 1,4-butanediol, bisphenol A, etc., and at least one compound that contains at least 2 carboxyl groups selected from the group consisting of maleic acid, adipic acid, phthalic acid, trimellitic acid, etc. Other examples include polyesters obtained from the ring-opening polymerization of a cyclic ester, such as d-valerolactone, e-caprolactone, etc., in the presence of an initiator that contains two hydroxy groups. In addition, dihydroxy polycarbonates obtained by the reaction of a diol such as 1,4-butane-diol, 6-hexanediol [see **Revision 2**], etc., with a diaryl carbonate, such as diphenyl carbonate, or a dihydroxy polycarbonate obtained by reaction with phosgene. Further examples include dihydroxy polyacetals obtained from 1,6-hexanediol and formaldehyde or from 4,4'-dihydroxyethoxydiphenylmethyl-methane and formaldehyde. And still other examples include low-molecular-weight diols such as ethylene glycol, diethylene glycol, butanediol, neopentyl glycol, hexanediol, etc.

Of course the polyhydroxy compounds that contain at least 3 functional groups may consist of only those with more than 3 hydroxy groups.

If the average molecular weight of (a) the polyhydroxy compound with at least 3 functional groups is too high, the polyurethane as a rubber is not sufficiently repelled and the dispersion of the isocyanate-terminated prepolymer in water becomes difficult. If the average molecular

weight of (a) the polyhydroxy compound with at least 3 functional groups is too low, the polyurethane becomes hard and therefore its use where rubber elasticity is required may not be possible. Accordingly, it is preferable to use a polyhydroxy compound with at least 3 functional groups that has an average molecular weight of from about 100 to about 10,000, and preferably from about 200 to about 8,000.

In the monohydroxy polyalkylene oxide which is constituent (b) used in the aqueous polyurethane emulsion, 50-100% by weight of the polyoxyalkylene chain is composed of oxyethylene units, and from the standpoint of emulsifiability of the prepolymer and the physical properties of polyurethane, the molecular weight is preferably 400-8,000. This constituent is typically hydrophilic and can be obtained using a known method. Representative examples include polyoxyethylene glycol monomethyl ether, polyethylene glycol monoethyl ether, polyethylene glycol monobutyl ether, polyoxyethylene polyoxypropylene glycol monomethyl ether, etc. An OH group is at one terminal and a group which does not react with isocyanate is at the other terminal. These monohydroxy polyalkylene oxides can be used singly or in combinations of two or more. When the amount of monohydroxy polyalkylene oxide introduced into the polyurethane is small, the stability of the emulsion tends to be insufficient. And if the amount of monohydroxy polyalkylene oxide introduced into the polyurethane is excessive, the overall performance of the polyurethane tends to become poor. The amount of monohydroxy polyalkylene oxide to be introduced into the polyurethane varies from one kind to another, the type of polyhydroxy compound, the molecular weight, etc., however, it is preferable to introduce about 2 to about 40% by weight based on the sum of the amount of monohydroxy polyalkylene oxide and the amount of the polyhydroxy compound with at least 3 functional groups.

The sum of the average number of functional groups of all the polyhydroxy compounds and the monohydroxy polyalkylene oxide of (b) used in the present invention influences the performance of the polyurethane. If the average number of functional groups is too small, then the physical properties, chemical resistance, and heat resistance of the polyurethane become poor; whereas if the number of functional groups is too high, then the physical properties, especially the elongation of the polyurethane, become poor. It is preferable to combine all the polyhydroxy compounds and the monohydroxy polyalkylene oxide of (b) in such a way that the average number of functional groups is generally about 1.8 to about 3.0, and preferably about 2.1 to about 2.6.

With regard to the polyisocyanate which is constituent (c), known polyisocyanates which are typically used in the production of polyurethane are suitable for use. For example, polyisocyanates with a molecular weight of 130-1,000 are suitable for use. Aliphatic or aromatic polyisocyanates can be used singly or in combinations of two or more.

Representative examples of suitable polyisocyanates include tolylene diisocyanate, 4,4'-biphenylmethane diisocyanate, xylylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, lysine diisocyanate, 1,4-cyclohexylene diisocyanate, methylenebis(4-cyclohexyl isocyanate), isophorone diisocyanate, 1,5-naphthalene diisocyanate, etc. And triisocyanates such as lysine triisocyanate, triphenylmethane triisocyanate, etc., biuret products with hexamethylene diisocyanate, adducts formed by the addition of hexamethylene diisocyanate or tolylene diisocyanate to a polyol such as trimethylolpropane, etc., can also be used.

With regard to the chain extender which is constituent (d), various known chain extenders used in the production of polyurethane may be used. Representative chain extenders include polyhydroxy compounds, polyamines, etc. Polyhydroxy compounds which are chain extenders can be the polyhydroxy compounds which are the same as those polyhydroxy compounds described in (a), however, it is preferable that the polyhydroxy compounds used as chain extenders are used only in partial chain extension reactions. The polyamines are those with a molecular weight of 17-500, such as primary or secondary diamines. Suitable representatives of these polyamines include ethylenediamine, hexamethylenediamine, toluenediamine, xylenediamine, diaminodiphenylmethane, diaminocyclohexylmethane, piperazine, isophoronediamine, etc., which are adipatic, alicyclic, and aromatic diamines. In addition, compounds with at least 3 functional groups such as lysine 2-aminoethyl ester, diethylenetriamine, triethylenetetramine, etc., which are polyamines, ammonia, hydrazine, dihydrazines, amino acid hydrazines, etc.

Among the chain extenders, for those which are insoluble in water, it is preferable that they are used in partial chain extensions only as in the case of polyhydroxy compounds. Of course other chain extenders which can be used for partial chain extension can also be used.

The present aqueous polyurethane emulsions can be prepared by the reaction of (a) a polyhydroxy compound that contains at least 3 functional groups and (b) a monohydroxy polyalkylene oxide with a molecular weight of 400-8,000 in which 50-100% by weight of the polyoxyalkylene chain is an oxyethylene chain with (c) a polyisocyanate. The resulting substantially isocyanate-terminated prepolymer is dispersed in water with a small amount of an emulsifier if necessary, followed by reaction of the prepolymer with (d) a chain extender, or the chain of the prepolymer is partially extended and then the prepolymer is dispersed in water with a small amount of an emulsifier if necessary, followed by reaction of the prepolymer with (d) a chain extender.

The preparation of a substantially isocyanate-terminated prepolymer can be carried out using an isocyanate in the presence or absence of an inert solvent such as toluene, methyl ethyl ketone, ethyl acetate, trichloroethylene, etc., at a reaction temperature of generally about 50 to 130°C, however, in case a solvent is used, it is necessary to remove the solvent by a later process. In order to accelerate the reaction, a known catalyst such as a tertiary amine or tin compound may be used.

A mixture of (a) a polyhydroxy compound with at least 3 functional groups and (b) a monohydroxy polyalkylene oxide can be reacted with (c) a polyisocyanate, or in advance (a) a polyhydroxy compound with at least 3 functional groups may be reacted with (c) a polyisocyanate and then (b) a monohydroxy polyalkylene oxide can be added and reacted. However, the former method will more easily produce a substantially isocyanate-terminated prepolymer. An equimolar amount of polyisocyanate can be reacted with (b) a monohydroxy polyalkylene oxide and then reacted with (a) a polyhydroxy compound that has at least 3 functional groups to obtain a hydroxy-terminated reaction product, then a polyisocyanate can be added and reacted to obtain an isocyanate-terminated prepolymer. However, when this method is used, the reaction becomes complicated.

The amount of (c) polyisocyanate must be selected in such a way that all the hydroxy groups can react with the isocyanate groups. Namely, the ratio of the total number of isocyanate groups to the total number of hydroxy groups is preferably 1.2:1.0 to 4.0:1.0. Before the

prepolymer obtained in this way is dispersed in water, if necessary, it can be subjected to partial chain extension by reaction with (d) a chain extender at about 40°C to about 100°C. In this case, the amount of chain extender to be used should be limited to about one third molar equivalent or less of the remaining isocyanate groups of the prepolymer. If more than about one third molar equivalent of the chain extender is used, the viscosity of the prepolymer increases, thus making the subsequent emulsification process more difficult.

The prepolymer can be emulsified even when a typical emulsification device is used, however, an emulsification device such as a homogenizer or a colloidmin [see Revision 3], which can divide the existing particles into finer particles, is preferably used, thereby an aqueous emulsion that consists of smaller particles can be prepared.

The prepolymer per se can be dispersed in water, however, if a small amount of the emulsifying agent is used, then it (the emulsifying agent) can be added before the prepolymer is dispersed in water. The amount of the emulsifying agent to be used depends on the intended use of the polyurethane, however, generally speaking, it is 10 parts by weight or less, and preferably 5 parts by weight or less, based on 100 parts by weight of the prepolymer. For the emulsifying agent, one or a mixture of known emulsifying agents, anionic surfactants, cationic surfactants, and nonionic surfactants can be used.

The dispersion of an isocyanate-terminated prepolymer in water is preferably carried out at 90°C or less. The chain extender may be added either while the prepolymer is being dispersed in water or after the prepolymer is dispersed in water. When the chain extender is added, a chain extension reaction occurs. The chain extension reaction is typically carried out at about 90°C or less. Examples of chain extenders that can be used include water-soluble polyamines, ammonia, hydrazine, dihydrazines, amino acid hydrazides that are soluble in water, and those whose reactivity with isocyanate groups is high are preferable.

At the time of dispersing the isocyanate-terminated prepolymer in water, a portion of the isocyanate groups can be consumed by water, therefore it is preferable to use a chain extender whose amount is the equivalent or less of the remaining isocyanate groups in the prepolymer before its dispersion in water. And of course from the standpoint of stability and use of the emulsion, it is preferable that there is substantially no remaining isocyanate groups in the aqueous polyurethane emulsions which are the final products of the present invention.

In the aqueous polyurethane emulsions of the present invention, the proportion of polyurethane is generally 2-75% by weight, and preferably 5-60% by weight of the whole emulsion.

If necessary, various stabilizers, coloring agents, surfactants, etc., may be added to the aqueous polyurethane emulsions prepared in this way then they can be used as coating materials for paper and cloth, as paint, for the coating of metals, in artificial leather, as adhesives, etc.

The aqueous polyurethane emulsions of the present invention do not always need the use of an emulsifying agent, but even if a small amount of emulsifying agent is used, the emulsions obtained are stable. In other words, they are not affected all that much by emulsifying agents, which in essence solves the problem of deterioration of the working environment.

In the following, Actual Examples will be used to better understand the present invention, however, the present invention is not limited to these examples.

#### Actual Example 1

235 parts by weight of polyoxypropylene triol with an average molecular weight of 1,000, 59 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular weight of 400, 156 parts by weight of isophorone diisocyanate, and 0.04 part [see Revision 4] by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. Then they were reacted at about 85°C for 4 hours under a nitrogen gas stream to synthesize a prepolymer. Next, 120 g of the prepolymer was put in a 600-mL stainless steel vessel and while the prepolymer was being vigorously stirred with a homogenizer about 180 g of water was added over about 10 minutes to give an aqueous emulsion of the prepolymer. Immediately after, 105 g of a 2.35% by weight aqueous solution of hydrazine hydrate was added over about 5 minutes, then the resulting mixture was continuously stirred to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week [see Revision 5], however, no precipitates were observed [see Revision 6].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 79 kg/cm<sup>2</sup> and 540%, respectively.

#### Actual Example 2

100 parts by weight of polyoxybutylene glycol with an average molecular weight of 850, 56 parts by weight of polycaprolactone triol with an average molecular weight of 880, 56 parts by weight of polyoxyethylene polyoxypropylene glycol monomethyl ether with an average molecular weight of 2,050 in which 80% by weight of the polyoxyalkylene chain consisted of oxyethylene units and 20% by weight of the polyoxyalkylene chain consisted of oxypropylene units, 95 parts by weight of isophorone diisocyanate, and 0.05 [see Revision 7] part by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 65-90°C for about 5 hours under a nitrogen gas stream to synthesize a prepolymer. Then, while 90 g of the prepolymer was being vigorously stirred with a homogenizer, 260 g of water was added over about 10 minutes. Immediately after, 100 g of a 4.52% by weight aqueous solution of hexamethylenediamine was added dropwise over about 3 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week, however, no precipitates were formed [see Revision 8].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 85 kg/cm<sup>2</sup> and 500%, respectively.

#### Actual Example 3

197 parts by weight of Nippollan 4070 (Nippon Polyurethane Industry Co., Ltd.) with an average molecular weight of 2,000 which is a polyester diol, 19 parts by weight of polyoxyethylene glycol with an average molecular weight of 2,000, 67 parts by weight of polycaprolactone triol with an average molecular weight of 880, 67 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular weight of 2,000, 0.04 part by weight of dibutyltin dilaurate, and 99 parts by weight of isophorone diisocyanate were put in a

reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 85°C for about 4 hours under a nitrogen gas stream to synthesize a prepolymer. Then, while 120 g of the prepolymer was being vigorously stirred with a homogenizer, 280 g of water was added over about 15 minutes. Immediately after, 200 g of a 3.12% by weight aqueous solution of isophoronediamine was added over about 5 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week, however, no precipitates were observed.

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 185 kg/cm<sup>2</sup> and 880%, respectively. Nippolan 4070 is a polyester diol that consists of neopentyl glycol, hexanediol, and adipic acid.

#### Actual Example 4

291 parts by weight of polyoxypropylene triol with an average molecular weight of 3,000, 83 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular weight of 2,000, 76 parts by weight of isophorone diisocyanate, and 0.04 part by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 85°C for about 4 hours under a nitrogen gas stream to synthesize a prepolymer.

Then, while 120 g of the prepolymer was being vigorously stirred with a homogenizer, 280 g of water was added over about 15 minutes. Immediately after, 200 g of a 1.52% by weight aqueous solution of hexamethylenediamine was added over about 5 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week, however, no precipitates were observed [see Revision 9].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 37 kg/cm<sup>2</sup> and 490%, respectively.

#### Actual Example 5

170 parts by weight of polyoxypropylene diol with an average molecular weight of 1,000, 43 parts by weight of polyoxyethylene glycol with an average molecular weight of 2,000, 66 parts by weight of polyoxypropylene triol with an average molecular weight of 1,000, 19 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular weight of 2,000, 152 parts by weight of methylenebis(4-cyclohexyl isocyanate), and 0.04 [see Revision 10] part by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 85°C for about 4 hours under a nitrogen gas stream to synthesize a prepolymer.

Then, while 120 g of the prepolymer was being vigorously stirred with a homogenizer, 180 g of water was added over about 15 minutes. Immediately after, 180 g of a 3.22% by weight aqueous solution of hexamethylenediamine was added in about 5 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week [see Revision 11], however no precipitates were observed [see Revision 12].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 181 kg/cm<sup>2</sup> and 650%, respectively.

#### Actual Example 6

219 parts by weight of polyoxypropylene glycol with an average molecular weight of 2,000, 68 parts by weight of polyoxypropylene triol with an average molecular weight of 1,000, 68 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular weight of 2,000, 94 parts by weight of isophorone diisocyanate, and 0.04 part by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 85°C for about 4 hours under a nitrogen gas stream to synthesize a prepolymer. Then, while 120 g of the prepolymer was being vigorously stirred with a homogenizer, 280 g of water was added over about 15 minutes. Immediately after, 200 g of a 2.01% by weight aqueous solution of hexamethylenediamine was added over about 5 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week, however, no precipitates were observed [see Revision 13].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 53 kg/cm<sup>2</sup> and 100%, respectively.

#### Actual Example 7

187 parts by weight of polycaprolactone diol with an average molecular weight of 770, 77 parts by weight of polyoxypropylene triol with an average molecular weight of 1,000, 66 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular weight of 2,000, 121 parts by weight of hexamethylene diisocyanate, and 0.03 [see Revision 14] part by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 65-85°C for about 4 hours under a nitrogen gas stream to synthesize a prepolymer.

Then, while 120 g of the prepolymer was being vigorously stirred with a homogenizer, 280 g of water was added over about 15 minutes. Immediately after, 200 g of a 5.19% by weight aqueous solution of isophoronediamine was added over about 5 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week [see Revision 15], however, no precipitates were observed [see Revision 16].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 114 kg/cm<sup>2</sup> and 400%, respectively.

#### Actual Example 8

247 parts by weight of polyoxypropylene glycol with an average molecular weight of 2,000, 55 parts by weight of polyoxypropylene triol with an average molecular weight of 1,000, 64 parts by weight of polyoxyethylene glycol monomethyl ether with an average molecular

weight of 2,000, 91 parts by weight of isophorone diisocyanate, and 0.04 part by weight of dibutyltin dilaurate were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas-feeding tube. They were then reacted at about 85°C for about 4 hours under a nitrogen gas stream to synthesize a prepolymer.

Then, while 120 g of the prepolymer was being vigorously stirred with a homogenizer, 280 g of water was added over about 15 minutes. Immediately after, 200 g of a 2.09% by weight aqueous solution of isophoronediamine was added over about 5 minutes, then the stirring was continued to give an aqueous polyurethane emulsion. The emulsion was left to stand for one week, however no precipitates were observed [see Revision 17].

After the emulsion was dried, it was heated at 140°C for 20 minutes. The tensile strength and elongation of the film obtained in this way were 48 kg/cm<sup>2</sup> and 1,000% or greater, respectively.

## FORM FOR PROCEDURAL REVISION

September 10, 1980

To: Mr. Haruki Shimada, Head of the Patent Office

1. Matter to be Revised: Patent Application No. 55[1980]-61,717

2. Title of the Invention:

AQUEOUS POLYURETHANE EMULSIONS AND A METHOD FOR THEIR PRODUCTION

3. Party Requesting the Revisions:

Relation with the Matter Involved: Patent Applicant

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Name: Toray Industries, Inc.

President: Masao Ikawa

4. Date of the Order for Revision:

Voluntary

5. Number of Inventions Increased by the Revisions:

None

6. Subject of the Revisions:

"Detailed Description of the Invention" of the "Specification"

7. Contents of the Revisions:

(1) The "and a common method" in line 19 of p. 6 of the specification is revised to "by a common method" in lines 25-26 of p. 5 of the English translation.

(2) The "6-hexanediol" in line 16 of p. 8 of the specification is revised to "1,6-hexanediol" in line 26 of p. 6 of the English translation.

(3) The "colloidmin" in line 17 of p. 7 of the specification is revised to "colloid mill" in line 21 of p. 11 of the English translation.

(4) The "0.04" in line 3 of p. 20 of the specification is revised to "0.03" in line 16 of p. 13 of the English translation.

(5) The "for one week" in line 11 of p. 20 of the specification is revised to "for one day" in line 1 of p. 14 of the English translation.

(6) The "no precipitates were observed" in line 12 of p. 20 of the specification is revised to "only a small amount of precipitates were observed" in lines 1-2 of p. 14 of the English translations.

(7) The "0.05" in line 7 of p. 21 of the specification is revised to "0.02" in line 13 of p. 14 of the English translation.

(8) The "no precipitates were formed" in line 15 of p. 21 of the specification is revised to "almost no precipitates were formed" in line 22 of p. 14 of the English translation.

(9) The "no precipitates were observed" in line 15 of p. 21 of the specification is revised to "almost no precipitates were observed" in line 12 of p. 16 of the English translation.

(10) The "0.04" in line 13 of p. 24 of the specification is revised to "0.02" in line 22 of p. 16 of the English translation.

(11) The "for one week" in line 20 of p. 24 of the specification is revised to "for one day" in line 6 of p. 17 of the English translation.

(12) The "no precipitates were observed" in line 1 of p. 25 of the specification is revised to "almost no precipitates were observed" in line 7 of p. 17 of the English translation.

(13) The "no precipitates were observed" in line 1 of p. 26 of the specification is revised to "almost no precipitates were observed" in lines 24-25 of p. 17 of the English translation.

(14) The "0.03" in line 13 of p. 26 of the specification is revised to "0.02" in line 9 of p. 18 of the English translation.

(15) The "for one week" in line 1 of p. 27 of the specification is revised to "for one day" in line 18 of p. 18 of the English translation.

(16) The "no precipitates were observed" in line 2 of p. 27 of the specification is revised to "almost no precipitates were observed" in line 19 of p. 18 of the English translation.

(17) The "no precipitates were observed" in line 2 of p. 28 of the specification is revised to "only a small amount of precipitates were observed" in line 13 of p. 19 of the English translation.